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MAGNETOTHERMAL PROPERTIES OF SINGLE CRYSTAL DYSPROSIUM

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ABSTRACT

The magnetocaloric properties (the adiabatic temperature change) of the high purity single crystalline dysprosium have been measured directly over the temperature range from 78 to 220 K in magnetic fields from 0 to 14 kOe applied along the easy magnetization direction (*a*-axis). These results are in good to excellent agreement, except for two regions (105 to 127 K, and 179 to 182 K), with the previous magnetocaloric effect data reported on lower purity dysprosium samples. The magnetic phase diagram of Dy has been refined based on the results of these measurements and two new high magnetic field phases have been identified.

INTRODUCTION

The rare-earth metal dysprosium, Dy, has one of the largest magnetic moments in the lanthanide series, i.e., the experimentally determined value of the effective magnetic moment of a free Dy³⁺ ion is 10.83 μ_B [1]. In zero magnetic field Dy is paramagnetic (PM) above ~ 180 K, and its ordered magnetic structures include helical antiferromagnet (AFM) below $T_N = \sim 180$ K and a ferromagnet (FM) below $T_C = \sim 90$ K with the easy magnetization direction coinciding with the crystallographic *a*-axis [1,2]. At elevated magnetic fields, an intermediate fan magnetic structure is found in the temperature range between ~ 130 and ~ 180 K [2]. There is a tricritical point on the H-T phase diagram of Dy near 165 K [3] in a magnetic field of approximately 5 kOe, where the first-order AFM-fan transition becomes a second-order phase transformation. It is commonly accepted that in zero magnetic field the transition between the AFM and FM phases of Dy is a first order phase transformation, which is accompanied by a hexagonal-orthorhombic lattice

distortion, while the transition between the AFM and PM phases is a second order phase transformation.

The zero magnetic field AFM structure of dysprosium is a modulated spiral with the wave vector oriented along the hard magnetizing direction. The investigation of thermal expansion and sound propagation [4] shows the presence of commensurability points, where the wave vector of the helix structure becomes commensurate with the c -lattice parameter. Most of the anomalies of the magnetic structure of Dy were confirmed by neutron scattering [5], and are associated with the peculiar temperature dependence of the helix turn-angle.

Experimental results available to date show that Dy also behaves unusually in the vicinity of its Néel temperature [6,7]. Neutron scattering studies [8] confirmed the absence of a discontinuity near the AFM-PM transition. Concurrently other results [9] revealed the existence of a magnetic satellite peak near the Neel point in the direction of the c -axis. This observation was explained by either the presence of an intermediate vortex state or by the commensurability of both magnetic and crystal structures. The suggestion that the AFM – PM magnetic phase transition in Dy is a second order phase transformation has been confirmed by many experimental results [10]. The AFM-fan transition takes place over a broad range of magnetic fields and, thus, has a continuous character. The absence of a magnetic field hysteresis in the temperature range extending from the tricritical point to the Néel temperature also proves that this transition is a second order phase transformation. On the other hand, the presence of the temperature hysteresis of the magnetization near T_N (see [7]) and a number of other experimental data, collected in the vicinity of Néel temperature (e.g., see Ref. 11), provide some evidence for the first-order nature of this phase transition, and also resulted in claims that the AFM – PM transition has the characteristic of a mixed order phase transition.

The presence of the extended temperature hysteresis in the paramagnetic region suggests the possibility that AFM clusters exist in the bulk of the PM phase well above Néel temperature. Both the amount and size of these clusters decrease with increasing temperature, and Dy becomes truly paramagnetic and homogeneous only at temperatures 30 to 50 K above T_N (e.g., see Ref. 11). Since impurities may have strong effect on the nature of the phase transitions and, in principle, lead to the appearance of hysteresis in the vicinity of T_N , we carried out a detailed investigation of the phase diagram of Dy using high purity single crystals. Furthermore, it appears that first order phase transition materials, where the magnetism and the crystallography change simultaneously, hold a great promise as advanced magnetic refrigerant materials [12-14]. Therefore, this work is also an attempt to gain a better understanding of the behavior of the magnetocaloric effect (MCE) during a first-order phase transformations and the influence of the impurities on the MCE values.

EXPERIMENTAL DETAILS

The high-purity single crystals of dysprosium were prepared by the Materials Preparation Center of the Ames Laboratory. The overall purity of the samples was 99.98 wt %. The sample of Dy used in this study was cut in the form of a parallelepiped from a large grain. The approximate dimensions of the parallelepiped were $1 \times 3 \times 12$ mm³ with the longest side parallel to the a crystallographic axis. The orientation of the sample

was established by using a back-reflection Laue technique. The direct measurements of the MCE were performed with the magnetic field applied along the long side of the parallelepiped. The combined accuracy of the alignment of the a crystallographic direction with the direction of the applied magnetic field was of the order of $\pm 5^\circ$. The magnetocaloric effect was measured in the temperature interval from 78 K to 350 K in a quasistatic magnetic field. The magnetic field, which ranged from 0 to 14 kOe, was created around a thermally insulated specimen by charging and discharging the coil of an electromagnet. Due to the relatively large magnetic induction, the field sweeps from 0 to 14 kOe were performed during about 5 s. The quality of the thermal insulation of the sample was high enough to ensure nearly adiabatic conditions during the measurements. The equilibrium temperature of the sample was measured by a copper-constantan thermocouple before and after the magnetic field sweep. The MCE was determined as the difference between these two equilibrium temperatures. The relative experimental errors were estimated to be on the order of 7%. Most of the MCE results presented below were corrected for the demagnetizing field using the values of the demagnetizing factor for an ellipsoid with the same dimensions ($N = 0.17$). In some cases the magnetocaloric effect was measured both during heating or cooling of the sample. Measurements were carried out on cooling when each temperature (in zero magnetic field) was reached during cooling the sample from ~ 230 K to the target temperature, while in the case of heating, the target temperatures were reached during heating the sample, which had been initially cooled to ~ 77 K.

RESULTS

The isothermal dependencies of the MCE in the vicinity of the FM-AFM transition with the magnetic field applied along the easy magnetizing direction are shown in Fig.1. In

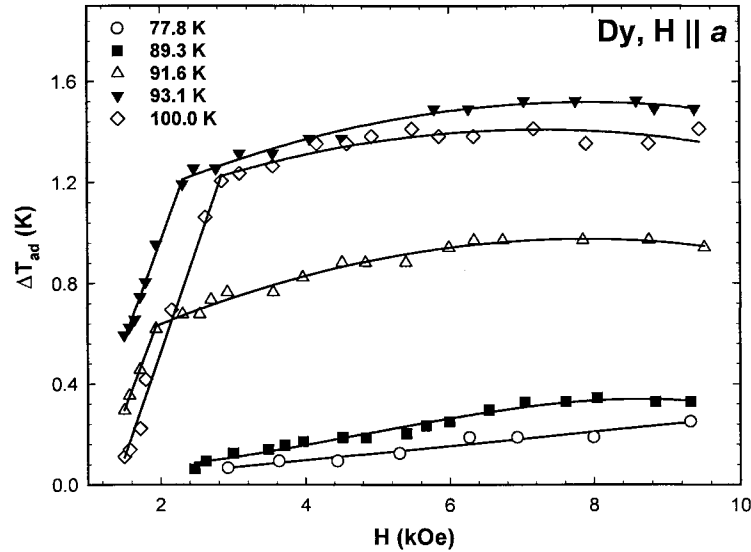


FIGURE 1. The isothermal dependencies of the magnetocaloric effect (corrected for demagnetization) in the single crystal Dy with the magnetic field applied along the easy magnetizing direction in the temperature interval from 77 to 100 K. The lines drawn through the data points are the guides for an eye.

the ferromagnetic region, i.e. at $T = 77.6$ and 89.3 K, the MCE is small and it increases nearly linearly with increasing magnetic field between ~ 2 and ~ 10 kOe. At higher temperatures, when Dy becomes antiferromagnetic in the zero magnetic field, the magnetocaloric effect shows quite different behavior. First, a rapid increase of the MCE is observed in low magnetic fields (2 to 3 kOe), and then the MCE is nearly saturated in magnetic fields exceeding ~ 4 kOe between 91.6 and 100 K. This behavior can be understood if one recalls that the magnetic field induces a first-order AFM \rightarrow FM transition above ~ 90 K in Dy. The first step-like increase and the saturation of the MCE is observed at 91.6 K; and this temperature agrees well with all previous data confirming that Dy is antiferromagnetic in zero magnetic field above ~ 90 K.

Typical isothermal dependencies of the MCE in the region from 110 to 127 K with the magnetic field applied parallel to the easy magnetizing direction are shown in Fig. 2. Each MCE function shows two step-like anomalies. The first anomaly is due to a magnetic field induced AFM \leftrightarrow FM transition. The second step appears only above ~ 105 K. The difference between the values of the critical magnetic field corresponding to the first step as measured during the heating and cooling of the sample indicates the presence of a temperature hysteresis, which is expected during the metamagnetic AFM \leftrightarrow FM transitions. However, the values of the critical field corresponding to the second step remain essentially the same when measured during both the heating and cooling of the sample. We conclude, therefore, that first critical fields correspond to a first order phase transition, and that second critical fields are indicative of a second order phase transition. The magnetocaloric effect was practically completely reversible in the range of magnetic fields where the second step was observed.

Figure 3 illustrates the magnetocaloric effect in Dy as a function of temperature between 77 and 210 K in magnetic field varying from 0 to 10 kOe shown together with the previously reported data obtained using different purity single crystals of Dy. The general

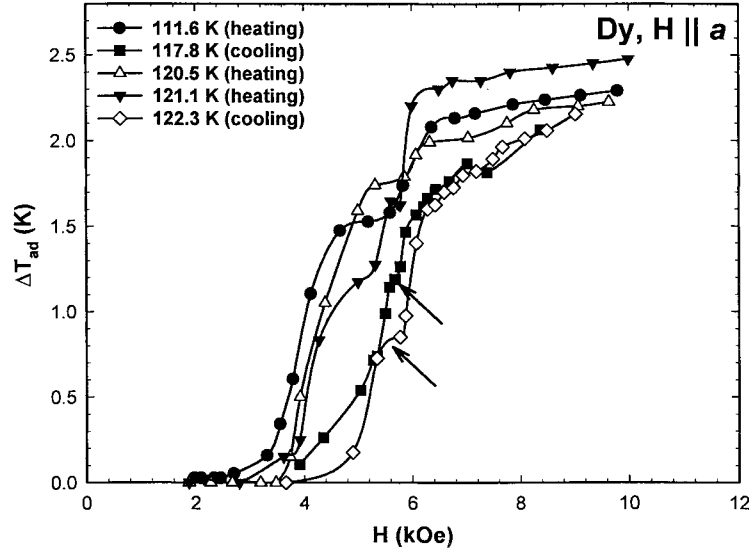


FIGURE 2. The isothermal dependencies of the magnetocaloric effect (corrected for demagnetization) in the single crystal Dy with the magnetic field applied along the easy magnetizing direction in the temperature interval from 110 to 125 K. The lines drawn through the data points are the guides for an eye.

behavior of the MCE is in a fair agreement with the earlier measurements except for the much sharper increase of the MCE around 90 K, and the much higher values of the MCE between ~ 180 and 210 K where they exceed those reported earlier [3,11] by about a factor of two. Note, that all data presented in Fig. 3 have not been corrected for the demagnetizing factor.

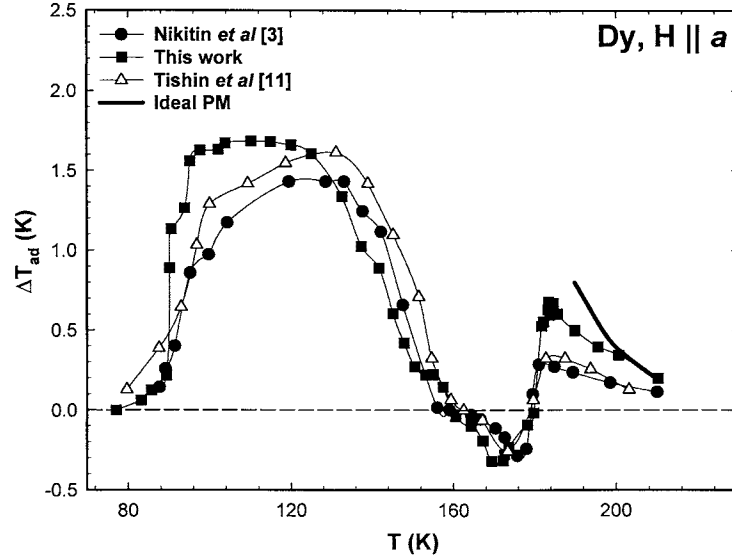


FIGURE 3. The magnetocaloric effect in the single crystal Dy in the 10 kOe magnetic field applied along the easy magnetizing direction compared with the earlier measurements [3,11]. All data are shown without correcting for demagnetization effects.

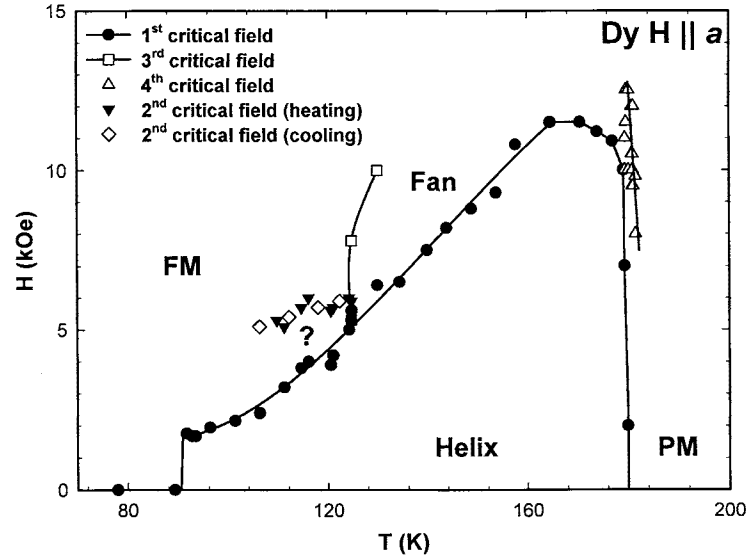


FIGURE 4. The H-T magnetic phase diagram of the single crystal of Dy along the easy a -axis constructed using the magnetocaloric effect data.

The magnetic phase diagram of Dy with the magnetic field applied along the easy magnetization direction based entirely on the magnetocaloric effect data is shown in Fig. 4. We note that the diagram includes points in temperature-magnetic field coordinates based on the anomalous MCE(T,H) behavior above ~ 120 K, which are not shown due to space limitations of this communication. The proposed phase diagram is similar to the earlier diagrams [2, 3, 5] with respect to the four major magnetic phases, i.e. PM, helix-AFM, fan, and FM structures, but some new and significant features on this diagram have been added. These include: (1) the first critical magnetic field separating helix-AFM and FM phase fields remains far above zero, at least down to 92 K, and then it is sharply reduced to zero between ~ 90 and 92 K; (2) additional phase fields delineating unknown magnetic phases between ~ 105 and ~ 127 K in magnetic fields between ~ 3 and 6 kOe and between ~ 179 and ~ 182 K in magnetic fields 8-12 kOe.

DISCUSSION

In general, most of the results reported above are in good agreement with those published earlier. Dy clearly behaves as a ferromagnetic material below its Curie point, and as an antiferromagnetic material between Curie and Néel points in zero magnetic field. There is an intermediate fan phase which forms during the transition from the AFM to FM phase in the temperature region above 127 K and in magnetic fields above ~ 5 kOe. From magnetocaloric effect we were able to detect the helix-AFM – fan phase transition only below ~ 130 K, because at higher temperatures the critical fields exceed the ~ 14 kOe limit of our electromagnet. According to the MCE data Dy clearly behaves as a paramagnet above ~ 182 K.

Contrary to earlier data, the MCE results obtained using high purity single crystal Dy indicate that there is a sharp increase of the critical magnetic field required to cause the helix-AFM to FM metamagnetic transition in the immediate vicinity of the Curie temperature, i.e. between 90 and 92 K (see Fig.4). It is feasible that this can be associated with the coexistence of both the helix-AFM and FM phases just above the Curie temperature.

In the region from 110 to 125 K a second step-like anomaly of the MCE is clearly distinguishable (see Figs. 2 and 4). We believe that results shown in Figs. 2 and 4 can be interpreted in terms of commensurability effects. Assuming that the magnetic and crystallographic lattices become commensurate at a certain combination of the magnetic field and temperature, this changes (increases) the symmetry of the system and thus may change the nature of the magnetic phase transition and may result in the splitting of the phase boundary line corresponding to a single first order phase transition between the helix-AFM and FM states into the two lines: the lower magnetic field phase boundary remains a first order phase transformation, while the higher magnetic field phase boundary becomes a second order phase transformation.

The anomalies of the magnetic field dependence of the MCE found in the temperature interval between 179 and 182 K correspond to the additional phase boundary line in the phase diagram (see Fig. 4). We assume that it reflects an intermediate “vortex” state that, as noted previously in the literature, may exist in this temperature region. Hence, the true Néel temperature of Dy when magnetic field is applied along its easy magnetizing direction is 182 K where all MCE anomalies, and therefore, critical fields no longer exist.

We also found a significant difference of the measured values of the MCE in the paramagnetic state in our high purity single crystal as compared with the previously reported data [3,11], see Fig. 3. The difference is well beyond the accuracy of the experimental measurements, i.e. the new results exceed the old results by about a factor of two. First, it is important to note that the biggest difference is observed at temperatures close to Néel temperature, i.e. where short range correlations (AFM clustering) are significant, and this difference diminishes when the temperature increases and the system approaches a truly paramagnetic state. The obtained results could be understood as follows.

To consider the influence of the antiferromagnetic clusters on the MCE values, one can calculate the magnetocaloric effect of dysprosium assuming an ideal paramagnetic behavior. It is well known that the magnetization, $M(H,T)$, of an ideal paramagnetic material follows Curie-Weiss law:

$$M(H,T) = \frac{Np_{eff}^2}{3k} \frac{H}{T - T_N}, \quad (1)$$

where N is the number of paramagnetic atoms, k is the Boltzmann constant, and $p_{eff} = g^2 J(J+1) \approx 10\mu_B$ is the effective magnetic moment for dysprosium. Our experimental temperature dependence of the heat capacity in the temperature interval above 190 K and in the range of magnetic fields 0 - 10 kOe has been approximated by the following equation [12]:

$$C(H,T) = 10^7 \left(25 + \frac{125}{T - 172} \right). \quad (2)$$

After integration of Maxwell thermodynamic relation for MCE, using equations (1) and (2) and neglecting the quantities proportional to $(\Delta T_{ad})^2$, which is valid for small magnetic field change when the MCE is small, one can obtain the numerical expression for the magnetocaloric effect in a paramagnetic Dy:

$$\Delta T_{ad}(T) = 1.8 \frac{T}{(T - 172)(T - 167)}. \quad (3)$$

The results obtained using Eq. 3 are shown in Fig. 3 as a heavy solid line. As one can see, the calculated MCE values are in an excellent agreement with the results obtained in this work in the range of temperatures above 200 K. The earlier MCE data continue to deviate from the calculated ones over a much larger temperature range. Consider a model, where the magnetic field first suppresses AFM structure of each cluster and aligns their magnetic moments with the direction of the field. After that, the magnetism inside the clusters should become quite similar to that in the PM phase and, most likely, clusters no longer behave as a separated magnetic sub-phase. It is therefore expected that initial process of the transformation of AFM clusters results in negative ΔT and the total MCE value at low magnetic fields is thus reduced. Obviously, in the case of low purity samples there are more AFM clusters and the initial magnetization process leads to a larger reduction of the resulting MCE. Fundamentally, this difference is expected to be less

pronounced in higher magnetic fields and it is reasonable to conclude that in our (higher purity) sample, AFM clusters exist over a narrower temperature interval, than in case of previous studies. Unfortunately, the purity of the Dy sample investigated in [3,11] is unknown and it is difficult to carry out a more careful analysis of the observed differences.

CONCLUSIONS

The magnetocaloric effect in a single crystal Dy have been measured from 78 to 220 K in magnetic fields ranging from 0 to 14 kOe applied along the easy magnetizing direction. In the maximum magnetic field of 14 kOe, the value of the MCE varies from -1.2 K at 175.5 K to 2.5 K at 115 – 120 K. The results of our measurements are in fair agreement with earlier data. Considerable disagreement with previous measurements is observed in the immediate vicinity of Néel temperature in the paramagnetic state, which is most likely associated with the higher purity of the specimen used in this study. The H-T phase diagram of Dy have been revised to reflect the presence of two unknown magnetic phases existing between ~105 and ~127 K in magnetic fields between ~ 3 and 6 kOe and between ~179 and ~182 K in magnetic fields 8-12 kOe, respectively.

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